

CATALYTIC HYDROTREATMENT OF HETEROATOM SPECIES IN SOUTH BANKO COAL LIQUID DISTILLATE OVER CARBON SUPPORTED NiMo CATALYST

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Abstract

Hydrotreatment of crude liquid oil produced from South Banko coal (SBCL) was carried out using alumina and carbon supported NiMo catalysts to find advantages of carbon support for up-grading coal liquid. Reactivity of representation sulfur, nitrogen and oxygen molecular species were measured to confirm the high activity of the catalyst against refractory species. NiMo supported on of ultrafine particle carbon black (Ketjen Black:KB) with extremely large surface area was found an excellent support for hydrotreatment catalyst to show much higher activity for the hydrodesulfurization(HDS), hydrodenitrogenation(HDN) and hydrodeoxygenation(HDO) of coal liquid than that of a commercial NiMo/Al₂O₃ catalyst.

Key words: coal liquids oil, hydrotreatment, carbon support catalyst

Introduction

As environmental protections become greater concern, it is very essential to treat hydrocarbons feed-stocks such as naphthas, middle distillate, gas oil, vacuum gas oil, vacuum resids, coal liquids to decrease the content of undesirable aromatic hetero atomic species. Noble metal catalysts, which are excellent for aromatics saturation, get fast poisoned by the sulfur and nitrogen compounds to lose their activity.

The support to replace alumina is one of targets approaches for this purpose. Carbon has been recognized an interesting support to showing higher catalytic activity for the HDS of thiophene than alumina support [1]. Such high activity of carbon-supported HDS catalyst has been attributed to the inertness of the carbon support as compared to the conventional alumina support [1]. Carbon has the additional advantage over other support of a great flexibility in the modification of both the porosity and surface area. Daly et al [2] have shown that the types of carbons affected the distribution of active sulfides on their surface. Vissers et al. [3] found that increasing of carbon surface area results in increasing HDS activity because of the lower sintering trend of the active phase. Schmitt and Castellion [4] also found that sulfides supported on carbon with larger mean pore size were more active for the HDS of gasoil. Drahoradova et al. [5] reported that NiMo on carbon showed higher hydrodenitrogenation (HDN) activity and lower inhibition of HDS activity with thiophene/pyridine feeds than alumina-supported NiMo. Mochida et al [6], also notified that nickel molybdenum sulfide supported on carbon (Ketjen Black) was more active for the hydrogenation of 1-methylnaphthalene than NiMo supported on alumina. Furthermore, carbon-based catalysts can be less expensive than alumina. Combustible carbon facilitates metals recovery and reduced volume of disposal [7].

The present study prepared KB supporting nickel-molybdenum sulfide catalyst and applied to the hydrotreatment of SBCL which contained much more aromatic and hetero atom species such nitrogen, sulfur and oxygen compounds. Its activity for hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO) was compared with those of a commercially available alumina catalyst to find the advantages of carbon support in the hydrotreatment of highly polar feed.

Experimental

Feed

The sample used were two different cutting point of SBCL (A: bp < 300 °C; B: bp 200 ~ 350 °C) which was prepared at 450 °C, 15 Mpa using limonite catalyst in a BSU (Bench Scale Unit) pilot plant of Nippon Brown Coal Liquefaction Co. Ltd. and was supplied by courtesy of NEDO. Their properties are listed in Table 1.

Catalyst

A commercially available NiMo/ Al₂O₃ (NiO; 2 wt%, MoO₃; 10 wt%), was used as a reference. Carbon supported NiMo catalyst was prepared in the laboratory. Some properties of carbon black (Ketjen Black:KB EC 600JD) provided by Mitsubishi Chemical Co. are summarized in Table 2. Nickel and Molybdenum salt were impregnated simultaneously using Ni(Ac)₂ and MoO₂-AA in methanol. Ni(Ac)₂ and MoO₂-AA dissolved in methanol were mixed to the slurry KB methanol and were dispersed by ultrasonic for 40 min. The mixture was heated up to 40 °C for 120 min, followed by evaporation to remove solvent under reduced pressure. The catalyst precursor was then dried at 120 °C for 12 h in vacuum. It was presulfided in a 5 % of H₂S/H₂ flow at 360 °C for 2 h prior to the reaction.

Hydrotreatment procedures

Hydrotreatment of South Banko coal liquid distillate was performed in a 50ml magnetically stirred autoclave. The ratio of catalyst to feed was 10 wt%, and 10 g of feed was used. Feed was charged in to the autoclave together with catalyst, and the autoclave was flush with nitrogen three times to replace air and was then filled with pure hydrogen. The initial pressure of hydrogen was 10 MPa. The reaction time was counted from the point when the reaction temperature was reached to the prescribed temperature. The hydrogenated product was collected from the autoclave with acetone. The liquid product was then separated from the catalyst by vacuum filtration. After removal of acetone, the hydrogenated product was analyzed by GC-AED to calculate the extent of HDS, HDN and HDO.

Results

GC=AED chromatographs of SBCL (A) before and after hydrotreatment at 360 °C over NiMo/Al₂O₃ catalyst are illustrated in Figure 1 ~ 3. Figure 1 shows high reactivity of sulfur species, which allowed them complete removal under this condition. Nitrogen exhibited the lower reactivity and still much remained after the reaction as shown in Figure 2. Pyridines were the most reactive among nitrogen species. The nitrogen species left in the hydrotreated oil were found as anilines, methyl-, dimethyl-, trimethyl-anilines, quinoline and indoles. The oxygen compounds were further less reactive than other heteroatoms species as shown in Figure 3. Most of phenols still remained after the hydrotreatment over NiMo/Al₂O₃ catalyst at 360 °C. Dibenzofuran appeared the most refractory species.

Figure 4 & 5 illustrate both reactivities of SBCL (B) in the hydrotreatment at 360 °C over NiMo/Al₂O₃ and NiMo/KB. SBCL (B) of higher boiling range carried much less reactive species such as 4,6-dimethyldibenzothiophene and dimethylcarbazoles. Hence their heteroatom removal was much slow than that of SBCL (A). The carbon-supported catalyst was found more active than alumina supported one, shows better removal all heteroatoms. The advantage of carbon support decreases in order of S > N > O removal.

Discussion

The reactivity of heteroatom species in SBCL (A) is defined clearly in the order of S > N > O. Sulfur was easily removed became smaller content and least refractory species such as 4,6-dimethyldibenzothiophene. Nitrogen species are less reactive than sulfur species. Among the nitrogen species, very basic nitrogen species were removed at lower temperature, their

preferential adsorption being suggested. Anilines and alkyl anilines were less reactive. Oxygen species especially benzofuran were very unreactive.

KB supported NiMo catalyst was found much more active than alumina supporting ones especially against refractory species. Large surface area and very fine grains help its high dispersion of active phases over the surface and among the heteroatom species of the catalyst particles. The number of active site is believed to depend on the extent of sulfurization. Medium strength of chemical interaction between active phase and carbon support may be favorable for complete sulfurization.

The acidic polar support has been believed to help hydrogenation and C-X cleavage. It clearly accelerates the deactivation by coking through strong absorption. Carbon is certainly expected less deactivated. More chemical modification of carbon can be the target of the next research.

References.

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Table 1 Elemental analyses of feed

Sample	b.p(°C)	C*	H*	N*	S**	O***	H/C
A	< 300	84.97	10.37	0.84	667	3.74	1.46
B	200 - 350	85.59	9.09	1.74	770	3.49	1.27

* : wt%, ** : ppm, *** : differences

Table 2 Some Properties of Ketjen Black

Surface area (m ² /g)	1270
Volatile matter (%)	0.7
PH	9.0
Particle size (nm)	30
Apparent density (g/L)	115
Ash (%)	0.1
Ni (ppm)	1.5
V (ppm)	30
Fe (ppm)	100
Cu (ppm)	1
Mn (ppm)	1

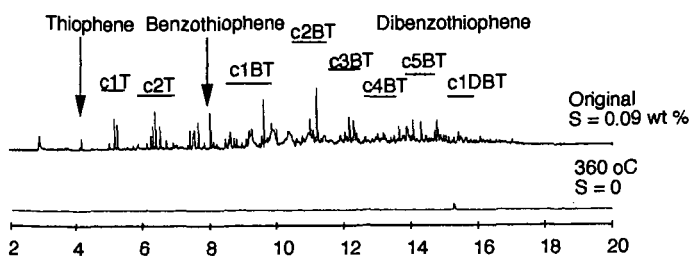


Figure 1 sulfur chromatograms of hydrotreated SBCL (A) over NiMo/Al₂O₃ catalyst

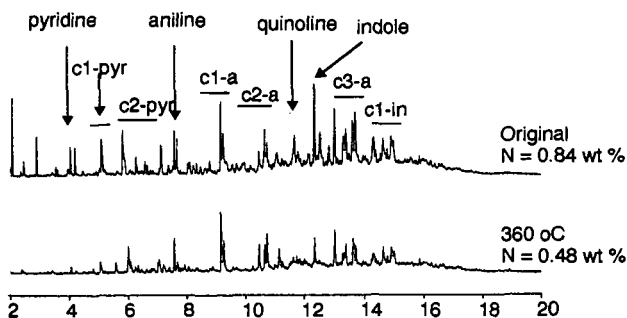


Figure 2 nitrogen chromatograms of hydrotreated SBCL (A) over NiMo/Al₂O₃ catalyst

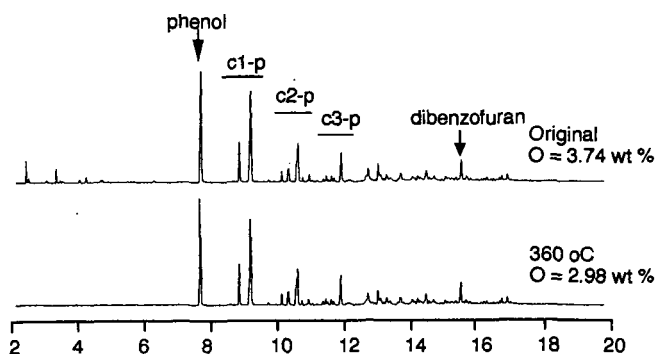


Figure 3 oxygen chromatograms of hydrotreated SBCL (A) over NiMo/Al₂O₃ catalyst

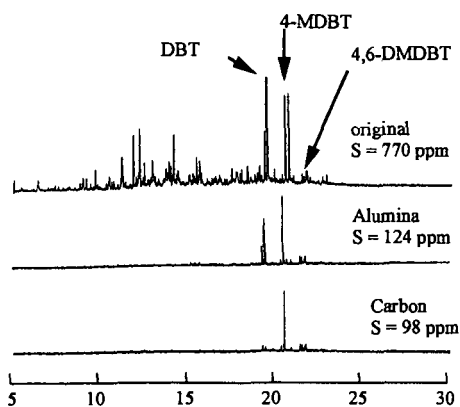


Figure 4 sulfur chromatogram of hydrotreated SBCL(B) over NiMo/Al₂O₃ and NiMo/carbon catalyst

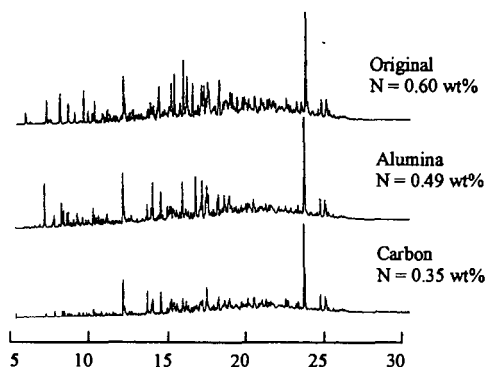


Figure 5 Nitrogen chromatograms of hydrotreated SBCL(B) over NiMo/Al₂O₃ and NiMo/carbon catalyst

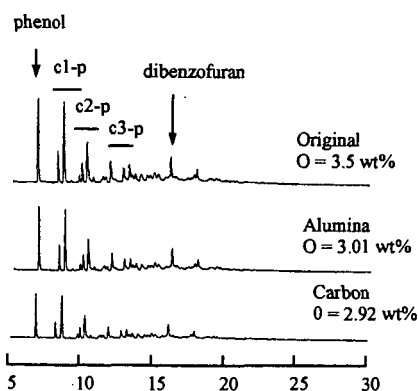


Figure 6 oxygen chromatograms of hydrotreated SBCL(B) over NiMo/carbon and NiMo/Al₂O₃ catalyst